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ELECTRONIC EXCITATION IN MOLECULAR COLLISIONS: STRUCTURAL, DYNA--ETC(U)
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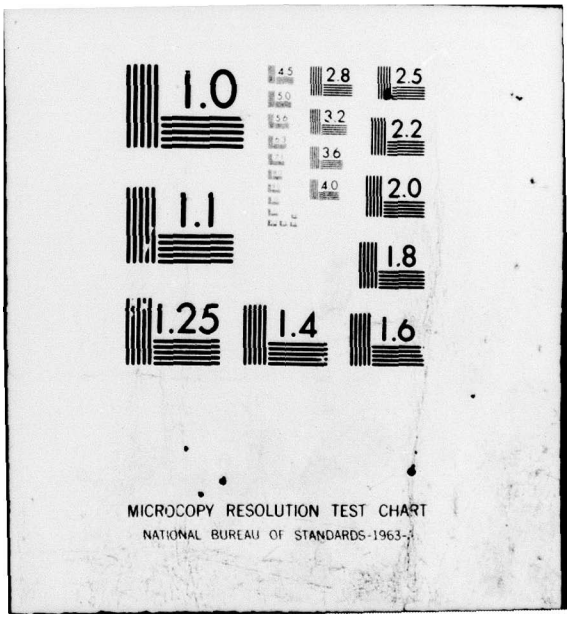
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Summary report for the first year.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Electronic energy, Potential energy surfaces, Branching ratio, Surprisal analysis, Information theory, Inversion procedures, Structure-reactivity correlations, Linear free energy relations.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The factors governing chemical reactivity with special reference to the role of electronic energy in promoting the reaction and to the production of electronically excited species are examined. The problem is studied both in general terms (i.e., the development of the required theoretical framework) and in application to specific systems.

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Annual Summary Report

Research Grant N-00014-78-G-0036

Electronic Excitation in Molecular Collisions: Structural, Dynamic and Kinetic Considerations

R. D. Levine

Principal Investigator

Contents*

*Arranged according to the 'Summary Questionnaire' of the ONR Physics Program

1. Principal Investigator

R. D. Levine

Professor of Physical and Theoretical Chemistry

The Hebrew University of Jerusalem.

2. Contract Description

The acquisition, storage and disposal of electronic energy by molecular collisions.

3. Scientific Problem

The factors governing chemical reactivity with special reference to the role of electronic energy in promoting the reaction and to the production of electronically excited species are examined. The problem is studied both in general terms (i.e., the development of the required theoretical framework) and in application to specific systems.

4. Technical Approach

Much of the work is based either directly or indirectly on the information theoretic approach to molecular collision theory, as pioneered and developed in Jerusalem.

5. Progress

During the first year much of the work has been directed at the development of the required theoretical tools. Progress to date can be summarised along the following lines.

a. Electronic potential energy surfaces.

The basis for a fundamental understanding of the dynamics of molecular collisions is the potential energy surface. We have

begun exploring two routes to the construction of such surfaces:

(a.1) Inversion of experimental data.

A general information theoretic algorithm for the inversion of data was developed*[3]. It is intended to apply this

*References are to the list of publications in paragraph 6 below.

approach to concrete problems during the second project year. The inversion algorithm [3] has however many other potential applications some of which may well be of direct interest to the Department of the Navy.** We therefore intend to explore

**Private communication from Dr. J. E. Shore, Naval Research Laboratory.

potentially significant implications of the approach even when these are not strictly within the technical description of the contract as given in paragraph 2.

(a.2) Semi-empirical approach

A semi-empirical approach procedure which has, thus far, given very accurate results has been developed [4]. Further work is in progress. The introduction of this method is based on work carried out to elucidate the systematics of chemical reactivity [1,4]. It is expected that developments in these two directions will continue to be mutually beneficial.

b. Chemical reactivity with special reference to branching ratios.

This direction is the major thrust of the project. Work has been carried out along several lines.

(b.1) The theory of branching ratios

The reactivity-selectivity principle has been derived on general grounds [6] and has been applied [7] to derive previous

theories (RRKM, the phase space theory, transition state theory, the unified statistical theory) and extension thereof. It is intended to use this formulation first in the analysis of experimental data and then as a predictive tool. In this connection, an explicit solution of a nontrivial dynamical problem by information-theoretic techniques was carried out [2].

(b.2) Structure-reactivity correlations

This is a semi-empirical version of (b.1) which has proven to be a versatile (cf. 5.(a.2) above) and useful tool [1,5] We expect to devote considerable attention to this development, even if it might lead us somewhat away from the strict technical description of the contract.

c. Surprisal analysis

Surprisal analyses for reactions which produce electronically excited diatomic molecules have been carried out and are in preparation for publication. A technically useful development has been the use of surprisal synthesis which enables one to place confidence limits and to simulate the chemiluminescent spectra.

d. Summary

The most significant work during the first year appears to be the development of the information-theoretic inversion algorithm (5(a.1)) and the semi-empirical structure-reactivity correlations (5(b.2)). We intend a follow-up of these directions in addition to other lines of enquiry as outlined in the original proposal.

6. Publications

a. Published papers

1. R. D. Levine, Free Energy of Activation: Definition Properties and Dependent Variables, J. Phys. Chem. 83, 159 (1979).

2. R. D. Levine and C. E. Wulfman, Energy Transfer to a Morse Oscillator, Chem. Phys. Letters 60, 372 (1979)

b. Papers accepted for publication

3. R. D. Levine, An Information Theoretic Approach to Inversion Problems, J. Phys. A.

4. N. Agmon and R. D. Levine, Empirical Triatomic Potential Energy Surfaces Defined Over Orthogonal Bond Order Coordinates, J. Chem. Phys.

5. N. Agmon and R. D. Levine, Structural Considerations in Chemical Kinetics: Gas Phase H-Atom Transfer Reaction Series, Is. J. Chem.

6. E. Pollak and R. D. Levine, The Reactivity-Selectivity Principle: The Derivation of Bounds and A Computational Study, J. Chem. Phys.

7. E. Pollak and R. D. Levine, Statistical Theories for Molecular Collisions: A Maximum Entropy Derivation, J. Chem. Phys.

Additional papers have been submitted but not yet accepted.

7. Special circumstances

Surprisal analysis for reactions producing electronically excited products was initially carried out by Dr. E. Keren (cf. paragraph 9 below). The quality of Keren's work and his rate of progress left much to be desired. He will be leaving us after a stay of ten months. The topic was assigned (6/79) to Mr. E. Zamir. Although inexperienced, he has done very well and we have recovered some of the lost time.

8. Budget

At the end of the first year we have some unspent but encumbered funds (e.g. page charges which are committed but not yet paid). There are no significant amounts of unspent funds.

9. Personnel

a. Prof. R. D. Levine, principal investigator. Awarded the Weizmann Prize*, April 1979 for his work on fundamental processes in chemical laser systems.

*Previous recipients include C. Pekeris (Applied Mathematics), Y. Nee'man (Elementary Particle Physics), E. Katzir (Biophysics) and M. Sela (Immunology) all of whom are members of the (US) National Academy of Science.

b. Dr. E. Pollak, senior postdoc. Previously with Professor P. Pechukas at Columbia. Left 7/31/79 to accept a tenure-track position.

c. Dr. E. Keren, postdoc. Previously with Prof. R. A. Marcus at Illinois. Started 12/1/78.

d. Mr. N. Agmon, advanced graduate student.

e. Mr. E. Zamir, beginning graduate student.

f. Mr. H. Almagor, programming assistant.

10. Other Current or Requested Federal Grants and Other Contract Support of R. D. Levine at the Hebrew University.

a. Studies in Molecular Disequilibrium

The US-Israel Binational Science Foundation, April 1979-April 1980, ~ $8000. J. L. Kinsey, I. Oppenheim, R. Silbey, and J. I. Steinfeld cooperating investigators.

b. Multiphoton Ionization

The US-Israel Binational Science Foundation, applied for April 1980 starting date but not yet approved. R. B. Bernstein cooperating investigator.

Both (a) and (b) are lower cost grants aimed primarily to enable the cooperating investigators to spend time with the research group of R. D. Levine in Jerusalem.